

Allyl Ethers of Carbohydrates. VI. Polymerization of Allyl Ethers

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The second paper of this series² presented data on the gelation time for a number of allyl ethers of polyhydroxy compounds. A rather guarded opinion was expressed regarding the relation between the number of allyl groups in the molecule and the gelation time of the ether, but more direct evidence on this subject was desirable. Experiments with mannitol of different degrees of allylation show clearly the difference in the rate of polymerization of these compounds. Another point of interest is the relation between the configuration and the polymerization rate of isomeric compounds. In the article cited, the gelation time of two such compounds—hexaallylmannitol (220 minutes) and hexaallylsorbitol (240 minutes)—seemed to be identical within experimental error. Similar results were obtained for another pair of isomeric compounds, allyl tetraallyl- α -D-glucoside (274 minutes) and allyl tetraallyl- α -D-galactoside (283 minutes).³ It seemed desirable, however, to verify this point with a larger number of compounds. Accordingly, besides some of those previously reported, a number of new compounds were made, such as allylated derivatives of erythritol, xylitol, arabitol, dulcitol, talitol and iditol,⁴ and their gelation time and the rate of oxygen absorption were measured. And finally some theoretical considerations regarding the polymerization of allyl ethers are presented.

To study the gelation of allyl-D-mannitol of different degrees of allylation, hexaallyl-D-mannitol was prepared as described previously.² Approximately tetraallyl-D-mannitol was prepared essentially by the same method but with less concentrated alkali, and 3,4-diallyl-D-mannitol was made by allylating 1,2:5,6-diisopropylidene-D-mannitol, and removing the isopropylidene groups by hydrolysis with dilute hydrochloric acid. Diallylmannitol is a crystalline compound.⁵ The gelation time for the three compounds was deter-

mined at 120° (above the melting point of diallylmannitol), with oxygen bubbling through at the rate of 7.5 liters per hour. The gelation time was 95 minutes for hexaallylmannitol, 165 minutes for the tetraallyl compound, and 425 minutes for the disubstituted mannitol. This clearly shows that increase in the degree of allylation (for the same compound) reduces the time of gelation.

The rate of oxygen absorption and the gelation time of various completely allylated sugar alcohols at 80° are given in Table I. All the figures in the table represent an average of two or more well agreeing results. It will be observed that with the increase of the chain from 3 to 6 carbons the gelation time decreased from 974 minutes for allyl glycerol to 900 for erythritol, to 602 for pentitols, and to 502 for the hexitols.

TABLE I
GELATION TIME AND OXYGEN ABSORPTION OF ALLYL ETHERS AT 80°

Compound	Gelation time	Oxygen absorption (micrograms per gram per minute)
Triallylglycerol	974	158
Tetraallylerythritol	900	83
Pentaallylxylitol	504	92
Pentaallyl-D-arabitol	700	91
Hexaallyl-D-mannitol	466	77
Hexaallyl-D-sorbitol	474	74
Hexaallyldulcitol	565	77
Hexaallyl-D-talitol	...	85
Hexaallyl-L-iditol	...	81

On the other hand, the rate of oxygen absorption decreased gradually (with the exception of erythritol) from 158 micrograms per gram per minute for glycerol to 92 for pentitols and 79 for hexitols. It is not clear at present why allylxylitol gels faster than allylarabitol or why allyldulcitol gels more slowly than either allylsorbitol or allylmannitol.

In a previous paper² Nichols and Yanovsky proposed a scheme based on the hydroperoxide theory of Criegee, Pilz and Flygare and of Farmer and Sundralingam to explain the oxidative polymerization of allyl ethers. It explained satisfactorily the presence of peroxide, epoxide⁶ and acrolein during oxidation of allyl ethers. In addition to these products, water appears during the process of gelation. Thus in one experiment 200 g. of hexallylmannitol was heated at 80°, while oxygen was passed through the liquid. The outgoing oxygen was led through two traps immersed in solid carbon dioxide-chloroform-carbon tetrachloride mixture. About 4.4 g. of liquid was collected

(1) One of the laboratories of the Bureau of Agriculture and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Nichols and Yanovsky, *THIS JOURNAL*, **67**, 46 (1945).

(3) Talley, Vale and Yanovsky, *ibid.*, **67**, 2037 (1945).

(4) Our thanks are due to Prof. C. S. Hudson and Dr. R. M. Hann of the National Institute of Health for samples of talitol, iditol, xylitol and arabitol, and to Prof. M. L. Wolf from of Ohio State University for a sample of xylitol.

(5) Incidental to the preparation of diallylmannitol, some monoallyl-D-mannitol was obtained, which from the method of preparation was judged to be 3-allyl-D-mannitol. Malaprade's reaction (*Bull. soc. chim.*, [4] **43**, 683 (1928); [5] **4**, 906 (1937)), was used to confirm the position of the substituent. A water solution of 0.5556 g. of the monoallylmannitol was treated with 20 ml. of 0.4070 *M* aqueous sodium metaperiodate and diluted to 50 ml. After three hours, 5 ml. and 20 ml. aliquots were titrated for periodate and formic acid, respectively. For each mole of monoallylmannitol, 3.24 moles of periodate were consumed and 1.12 moles of formic acid formed. Somewhat higher results than expected theoretically are due to a reaction between the periodate and the allyl group.

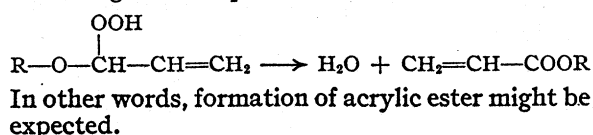
(6) Nichols, Wrigley and Yanovsky, *THIS JOURNAL*, **68**, 2020 (1946).

TABLE II
PHYSICAL AND ANALYTICAL DATA FOR ALLYL ETHERS

Compound	Yield, % of theoretical	Boiling point		Formula	n_D^{20}	d_4^{20}	Molecular refraction		Allyl, %		Carbon, %		Hydrogen, %	
		°C.	mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Tetraallylerythritol	57	102-104	0.01	C ₁₆ H ₂₀ O ₄	1.4590	0.9555	80.79	80.79	58.2	58.2	68.1	68.1	9.3	9.1
Pentaallylxylitol	65	125-127	.01	C ₂₀ H ₂₄ O ₅	1.4667	.9728	100.44	100.48	58.3	57.7	68.2	68.2	9.2	9.2
Pentaallyl-D-arabitol ^a	65	129-131	.01	C ₂₀ H ₂₄ O ₅	1.4662	.9756	100.44	100.10	58.3	58.3	68.2	68.1	9.2	9.1
Hexaallyldulcitol	60	128-130	.01	C ₂₄ H ₂₈ O ₆	1.4715	.9892	120.09	119.50	58.3	57.8	68.2	68.3	9.1	9.2
Hexaallyl-D-talitol	48	113-115	.01	C ₂₄ H ₂₈ O ₆	1.4695	.9810	120.09	120.06	58.3	58.1	68.2	68.4	9.1	8.9
Hexaallyl-L-iditol ^b	55	130-133	.01	C ₂₄ H ₂₈ O ₆	1.4705	.9831	120.09	120.03	58.3	58.0	68.2	68.4	9.1	9.1

^a $[\alpha]_D^{25}$ of an 8% solution in absolute alcohol, -3.5° . ^b $[\alpha]_D^{25}$ of an 8% solution on absolute alcohol, $+3.0^\circ$.

in the traps. The analysis showed that the liquid had about 60% acrolein and about 30% water. Clover⁷ found that hydroperoxides of ethers can break down, with the formation of an ester and water. In the case of ethyl benzyl ether hydroperoxide, the principal decomposition product was ethyl benzoate. It is evident that if a similar reaction takes place in allyl ethers, it will proceed according to the equation



This hypothesis was put to a test. Allylmannitol (113 g.) was heated at 80° while oxygen was passed through the liquid. The process was stopped at about three-quarters of the way to gelation. Determination of ester equivalent gave the figure 764, corresponding to 9.3% acrylate, or about 0.5 acrylate group per mole of the original allylmannitol. An attempt to identify the acrylic acid as its *p*-bromophenacyl ester was unsuccessful, perhaps because most or all of the acrylate was in a polymerized state. Acrylic ester, if present, probably takes part in the polymerization of allyl ethers.

Experimental

Preparation of 3,4-Diallyl-D-mannitol.—1,2:5,6-Diisopropylidene-D-mannitol was prepared according to directions of Baer.⁸ The crude product (m. p.; $116-117^\circ$ as compared with 122° for the recrystallized material) was used for the preparation of 3,4-diallyl-1,2:5,6-diisopropylidene-D-mannitol.

To a well-stirred mixture of 122 g. of diisopropylidene mannitol in 150 ml. of dioxane and 452 g. of allyl bromide heated at $80-85^\circ$, 298 g. of 50% sodium hydroxide solution gradually was added during thirty minutes. The heating and stirring was continued for six hours. The organic layer was dried with anhydrous sodium sulfate, and its volatile constituents were removed by distillation at atmospheric pressure. The residue was distilled *in vacuo*, and the fraction distilled at $110-118^\circ$ at about 1 mm. was collected. The yield was 132 g. of crude diallyl-diisopropylidene-mannitol.

Anal. Calcd. for C₁₈H₃₀O₆: allyl, 24.0; isopropylidene, 24.6. Found: allyl, 27.6; isopropylidene, 26.1.

Without further purification this substance was used for the preparation of diallylmannitol. One part of diallyl-diisopropylidene-mannitol was hydrolyzed in eight

parts of 50% alcohol containing 0.2% hydrochloric acid at 70° .¹⁰ After eight hours the hydrochloric acid was removed with silver oxide. The precipitate was filtered off and the filtrate evaporated to dryness, yielding 104 g. of crude diallylmannitol from 129 g. of crude diallyl-diisopropylidene-mannitol. The product was purified by dissolving one part in five parts of hot methyl alcohol. Eighteen parts of hot benzene and some decolorizing carbon were added. After removing most of the methyl alcohol by azeotropic distillation, the solution was filtered, and allowed to crystallize. After two recrystallizations a constant melting point, $111-112^\circ$ (cor.), was reached. Diallylmannitol is soluble in water, methyl and ethyl alcohol, pyridine and glacial acetic acid but insoluble in benzene, toluene, ether and hexane. $[\alpha]_D^{25}$ for a 4% solution was $+42.3^\circ$ in absolute alcohol and $+44.7^\circ$ in water.

Anal. Calcd. for C₁₂H₂₂O₆: hydroxyl, 25.9; allyl, 31.3; C, 54.9; H, 8.45. Found: hydroxyl, 26.4; allyl, 30.1; C, 54.8; H, 8.55.

Preparation of Monoallyl-D-mannitol.—Sixty grams of crude diallylmannitol was dissolved in 100 ml. of hot methyl alcohol, and the solution was clarified with decolorizing carbon. To the boiling solution 800 ml. of hot benzene was gradually added. Boiling was continued for a while after the entire amount of benzene was added. When the total volume was about 800 ml., the solution was allowed to crystallize. The next day 13.5 g. of crystals was filtered off. On further evaporation the solution yielded crystals of diallylmannitol. The 13.5 g. of crystals was dissolved in 80 ml. of boiling methyl alcohol to which 900 ml. of boiling benzene was added. On cooling, 6.5 g. of crystals was obtained, which on one recrystallization gave a constant melting point, $119-120^\circ$ (cor.); $[\alpha]_D^{25}$ for a 4% solution in water was $+15.8^\circ$. On further evaporation of the filtrate, 4.5 g. of diallylmannitol was obtained.

Anal. Calcd. for C₉H₁₈O₆: hydroxyl, 38.3; allyl, 18.5; C, 48.6; H, 8.16. Found: hydroxyl, 37.1; allyl, 18.1; C, 48.4; H, 7.94.

Preparation of Tetraallyl-D-mannitol.—Allylmannitol with approximately four allyl groups was prepared by adding gradually (half an hour) 448 g. of allyl bromide to a stirred and heated (75°) mixture of 56 g. of mannitol and 740 g. of 20% sodium hydroxide solution. The mixture was then stirred and heated for three hours more, after which it was worked up in the usual manner. It yielded 38% of the theoretical value of a product boiling at $159-162^\circ$ (1 mm.). Analytical results, 46.4% allyl and 11.2% hydroxyl, indicate the presence of 3.8 allyl groups.

Allylation of Polyhydric Alcohols.—Completely allylated sugar alcohols not described previously were prepared by the two-step method described in an earlier paper.² In some cases (talitol, for example, where only a small quantity of substance was available) a larger excess of allyl bromide was used to increase the volume of liquid for better stirring and handling. The physical properties and analytical results for these compounds are given in Table II.

(7) Clover, *THIS JOURNAL*, 46, 419 (1924).

(8) Baer, *ibid.*, 67, 338 (1945).

(9) Elsner, *Ber* 16, 2364 (1928).

(10) Irvine and Paterson, *J. Chem. Soc.*, 105, 898 (1914).

Determination of Water.—The water in the acrolein-water mixture was determined with acetylpyridinium chloride reagent.¹¹

Determination of Acrolein.—The acrolein was determined by the sulfite method.¹²

Determination of Ester Equivalent.—The ester equivalent was determined—by C. O. Willits and M. S. Gaspar of this Laboratory—by refluxing partially polymerized allyl ether with 0.2 *N* alcoholic sodium hydroxide, for one hour, continuing the refluxing for another hour after an equal amount of water had been added, and titrating the excess alkali electrometrically with 0.1 *N* acid.

Determination of Allyl Groups.—For completely substituted compounds the mercuric acetate modification of the Wijs method¹³ gave the most accurate results.

Acknowledgment.—The assistance of Mrs. M. F. Durchsprung in making Barcroft-War-

(11) Smith and Bryant, *THIS JOURNAL*, **57**, 841 (1935); also R. L. Shriner, "Quantitative Analysis of Organic Compounds," 1944, p. 40.

(12) Adams and Adkins, *THIS JOURNAL*, **47**, 1358 (1925); also, R. L. Shriner, *ref.*, 11, p. 46.

(13) Hoffman and Green, *Oil and Soap*, **16**, 236 (1939); also, Boyd and Roach, *Analytical Chemistry*, **19**, 158 (1947).

burg and allyl group determinations, and of Miss M. J. Welsh in making carbon and hydrogen analyses is acknowledged.

Summary

Completely substituted allyl ethers of erythritol, xylitol, arabitol, dulcitol, talitol and iditol were prepared. With the increase of the chain from three to six carbons, the gelation time decreased, from 974 minutes for allylglycerol to 900 for erythritol, to 602 for pentitols, and 502 for hexitols. On the other hand, the rate of oxygen absorption decreased with the increase of the length of carbon chain. The relation between the configuration and the time of gelation of isomeric allyl ethers is not quite clear. The possibility of the formation of acrylic ester during the oxidative polymerization of allyl ethers is suggested.

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